Interfacial Reaction Between Oxide Fillers and P_2O_5 Glass Matrix for Barrier Ribs in Plasma Display Panel

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Abstract
Phosphate glass system is expected to be useful as a lead-free material in many devices in plasma display panels (PDP). The present study is mainly focused on the evaluation of interface reaction between ceramic fillers and phosphate glass matrix for barrier ribs in PDP. The results suggest that properties of barrier rib depend on the crystallization behavior and interface reaction between the fillers and glass matrix.

1. Introduction
The barrier ribs in flat panel display devices, PDP (plasma display panels) which are made of composites of a large portion of glass and ceramic fillers (Al_2O_3, TiO_2 and ZnO) create a discharging area for high luminance, and also form a sub-pixel of the PDP by preventing electrical and optical cross-talking between neighboring cells. Barrier ribs with a height and width of ~160 and 100㎛, respectively, are produced by etching or photo-resist a thick film printed using the paste on a glass substrate. The barrier ribs are fired at a temperature between 550℃ and 580℃ and densification to dimensions of 120 and 80㎛ in height and width [1-3].

For use as the barrier rib materials, the glass should have a combination of physical properties required for PDP applications. Among the various required; lower sintering temperature, environmentally friendly materials, and selection of the ceramic fillers which is suitable in the quality which is demanded. Until now, the glass composition used are mainly glasses containing PbO>50mol%. However, the development of Pb-free glass system is required from the environment viewpoint, because of RoHS and WEEE regulations. The applications of bismate, boronzinc and phosphate glasses have the advantage of eco-materials and low sintering temperatures [4].

In fact, in terms of economic point and lowest firing temperature, the B_2O_3-BaO-ZnO and P_2O_5-SnO glass system have been considered [4-5].

Phosphate glass system with low melting temperature, high thermal expansion coefficient(α), low glass transition temperature(T_g) and softening temperature(T_d) are of increasing interest and desirable for many applications, which is expected to be most useful in the low melting glasses of PDP [3, 5]. However, the phosphate glasses generally exhibit poor durability in aqueous media and the hygroscopic nature of such glasses makes them unsuitable for practical applications [3-5]. Properties of barrier rib depends on filler types and the content of fillers. For the production of a new barrier ribs it is one of the main parts to control the interface of fillers and lead-free matrix. The present study is mainly focused on the evaluation of interface reaction between ceramic fillers and phosphate glass matrix for barrier ribs in PDP.

2. Experimental Procedure
For glass preparation of the matrix, all compositions (P_2O_5-SnO-ZnO-B_2O_3) were used as chemical pure reagents. The batch powders were dry mixed and melted in an alumina crucible in an electric furnace for 1 to 2 h in air at temperatures between 1000-1100℃. The samples were prepared by dry milling to give the frit with a mean particle size(d_{50}) of 1-2㎛. The frit was mixed with ceramic fillers (Al_2O_3, ZnO) and was fired at 550℃ for 30 min (see Table 1). The glass transition temperature (T_g) and crystallization peak of glass and glass-ceramic filler were determined using a differential thermal analyzer (Tg-DTA 8120, Rigaku, Japan).

Interface reaction was observed by measuring the weight change of fired samples as a function of immersion time in 90℃ de-ionized water solution. The dissolution rate was considered reliable of if the sample did not show visible cracking. Fired samples were characterized by scanning electron microscopy

(FE-SEM, JSM-6700F, Jeol, Japan) and X-ray diffraction.

Table 1 Batch of composition, the glass frit and ceramic fillers (Al_2O_3 and ZnO)

Specimens (wt%)	Frit	Filler ZnO	Filler Al_2O_3	Tg (℃)	Tds (℃)
A	100	-	-	441	487
B	80	-	20		
C	80	20	-		
D	80	15	5		

3. Results and Discussion

Results of DTA of phosphate glass and fillers are shown in Fig 1. The glass transition temperature was detected at 441℃ for both glass and glass-ceramic filler (Table 1). Tp2 of (c),(d) in Fig. 1 is different with Tp2 of (a) due to addition of filler(ZnO). Crystallization peak was detected in the DTA curve of glass, and the glass with fillers showed two crystallization peaks. DTA curves show two exothermal peaks (crystallization) by glass crystallization (Tp2) in Fig 1a and a reaction (Tp1) between glass and ceramic fillers (ZnO) in Fig 1c,d. No reaction between Al_2O_3 filler and glass matrix is found (Fig 1b).

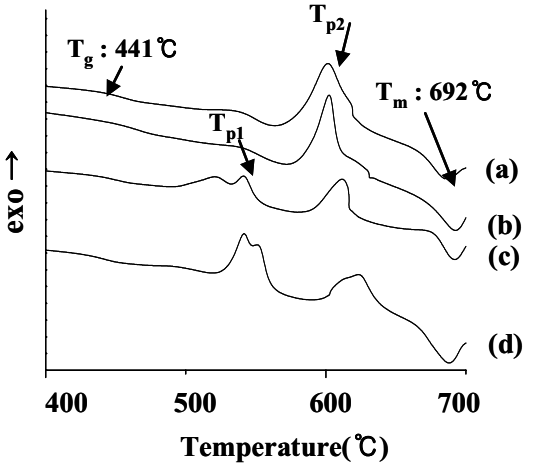

Figure 1 DTA curves of glass frit and fillers (Al_2O_3 and ZnO); (a) only frit (b) with 20Al_2O_3 filler (c) with 20ZnO filler and (d) with 5Al_2O_3 and 15ZnO filler (heating rate : 10℃/min)

For the fired samples, we analyzed the interface between the fillers and the glass matrix. The surface reaction seems to be related to the interface as shown in Cr1 and Cr3 in Fig. 2. It is observed that Cr1 crystalline phase by a reaction between glass and ZnO filler grow up from ZnO(white) filler to acicular (Fig 2c,d). Sn ion is in the glass matrix as a solid solution. Cr1(bright gray) is formed at part presumed as a residual glass matrix(Cr2). The crystals affected the formation of pores, which has an irregular shape rather than a spherical type appeared commonly in glass sintering. Figure 2(b) shows no indication of ion diffusion in the interface between Al_2O_3 filler and glass matrix (Fig 3b). A compared with the data of DTA and EDS, the peak (Tp1) is assumed as a Cr1 and Tp2 is assumed as a Cr3 (Fig 1).

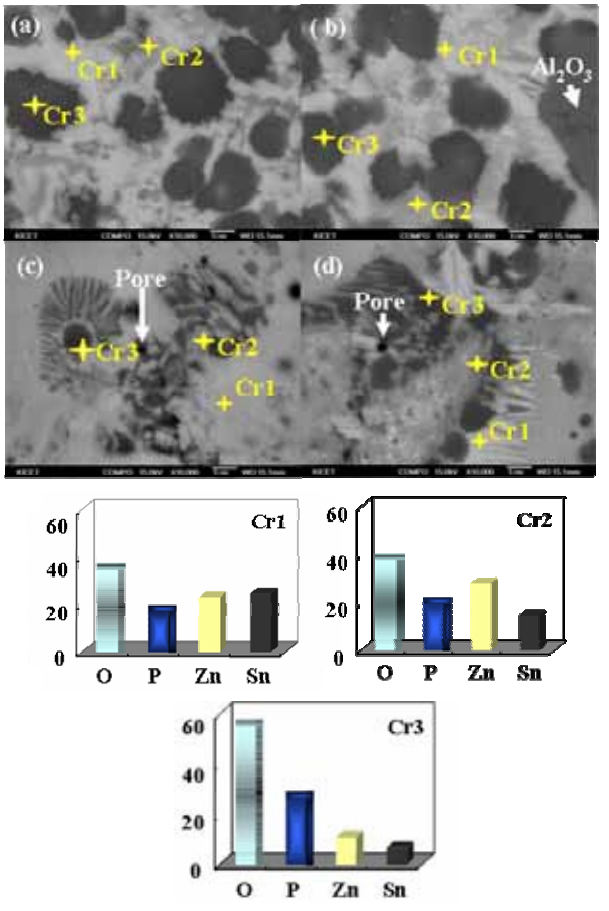

Figure 2 BSC image and EDS results of P_2O_5-ZnO-SnO-B_2O_3 glass system with fillers (Al_2O_3, ZnO); pellet were cold-pressed and sintered 30min in air at 550℃; (a)only frit, (b)20Al_2O_3 filler, (c)20ZnO filler, (d)5Al_2O_3 and 15ZnO filler; Cr1)bright gray, Cr2)gray, Cr3)dark gray

Crystalline phases such as BPO_4, $Zn_2P_2O_7$ and $Zn_3(PO_4)_2$ are observed by X-ray diffraction (Fig 3). The surface pores are caused by the formation of crystalline phases on the interface between the filler (ZnO) and glass matrix, generating a tensile stresses on the interface. As shown in Fig. 2 and Fig. 3, the crystalline phase appeared in the interface changes from $Zn_2P_2O_7$ and BPO_4 to $Zn_3(PO_4)_2$ with increasing the amount of ZnO filler. There are two crystalline phases detected as ZnO-P_2O_5($Zn_2P_2O_7$, $Zn_3(PO_4)_2$) with adding the amount of 20wt% filler(ZnO) as shown in Fig. 3(c). As compared with the data of XRD and EDS (B is not detected because of a property of EDS), Cr3 is assumed as a BPO_4 (Fig 3a,b) and the crystal phase of Cr1 is supposed to be zinc phosphates, $Zn_2P_2O_7$ and $Zn_3(PO_4)_2$, respectively.

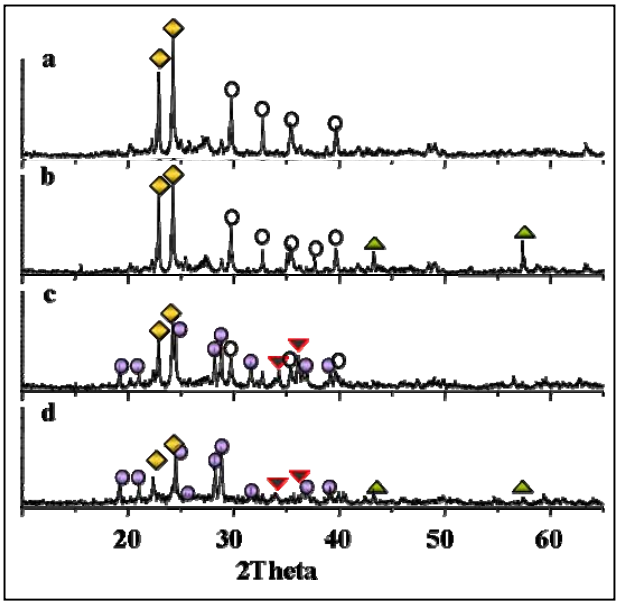

Figure 3 XRD patterns of the pellets (glass frit and fillers) were sintered at 550℃ for 30min. (a) only frit (b) with $20Al_2O_3$ filler (c) with 20ZnO filler and (d) with $5Al_2O_3$ and 15ZnO filler.

Dissolution of glass with fillers in aqueous solution is in Fig 4. The fired sample with only frit is strongly dissolved for the dissolution time, 10h. However, the fired sample with Al_2O_3 filler shows the poorest durability compared with others. in Fig 4. This is due to the formation of BPO_4 and $Zn_2P_2O_7$ in the glass matrix, which are easily dissolved in aqueous solution and unstrong interface reaction between Al_2O_3 and glass as shown in Fig. 4. The change of complex microstructure with new crystals is resulted from the reaction of the glass, P_2O_5-ZnO-SnO-B_2O_3 and ZnO filler, which weakly interacts with oxygen [4].

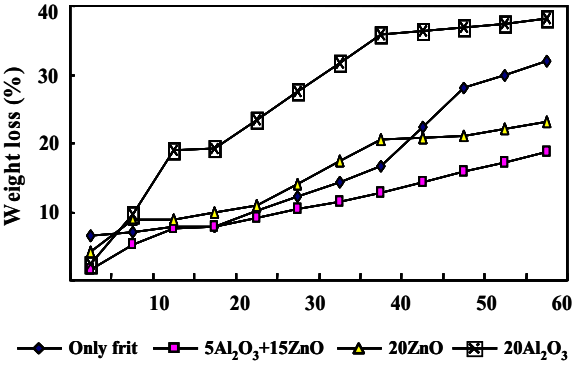

Figure 4 Weight loss of glass in de-ionized water at 90℃ versus time (0~60h)

4. Conclusion

Through analyzing the interface of the fillers (Al_2O_3, ZnO) and glass matrix, it is found that the chemical durability of composites was improved through the interface reaction. The change of complex microstructure with the new crystal ($Zn_3(PO_4)_2$ is resulted from the reaction. From the influence of individual fillers, the properties of barrier rib depend on the crystallization behavior and interface reaction between the fillers and glass matrix.

5. Acknowledgements

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6. References

[1] B. H. Jung, D. N. Kim, H. S. Kim, J. Non-Cryst. Solids 351 (2005)

[2] J. S. Jeon, E. G Chong and H. S. Kim, Proc. Int. J-K Seminar on Ceramic, 2005

[3] G. H. Hwang, H. J. Jeon and Y. S. Kim, J. Am. Ceram. Soc., 85(12) 2956-60 (2002)

[4] K. Morinaga, S. Fujino, J. Non-Cryst. Solids 282 (2001) 118-124

[5] R. Morena, J. Non-Cryst. Solids 263&264 (2000) 382-387